09/762619

JC ec'd PCT/PTO 09 FEB 2001

FLOTATION OF SULFIDE MINERAL SPECIES WITH OILS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. Provisional Application No. 60/096,175, filed August 11, 1998, which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

This invention relates to the beneficiating or concentrating of ores. In particular, this invention relates to collectors useful in ore beneficiating.

Flotation is a process for concentrating minerals from their ores. Flotation processes are well known in the art and are probably the most widely used method for recovering and concentrating minerals from ores. In a flotation process, the ore is typically crushed and wet ground to obtain a pulp. Additives such as flotation or collecting agents and frothing agents are added to the pulp to assist in subsequent flotation steps in separating valuable minerals from the undesired, or gangue, portion of the ore. The flotation or collecting agents can comprise liquids such as oils, other organic compounds, or aqueous solutions. Flotation is accomplished by aerating the pulp to produce froth at the surface. Minerals, which adhere to the bubbles or froth, are skimmed or otherwise removed and the mineral-bearing froth is collected and further processed to obtain the desired minerals.

The basic technique behind froth flotation is to use chemicals to increase the hydrophobicity of the mineral to be beneficiated to form a concentrate. Meanwhile, chemicals are added, as necessary, to decrease the hydrophobicity of unwanted (gangue) minerals, so that these minerals report to the slurry and are discarded as tail. The main alternative technique in froth flotation is "reverse flotation." This consists of floating the gangue minerals as a concentrate and keeping the mineral of interest in the slurry.

Chemicals that promote hydrophobicity of a mineral are called that mineral's "promoter" or "collector." Collectors based on fatty acids have long

been used in collecting one or more of the oxide minerals such as fluorspar, iron ore, chromite, scheelite, $CaCO_3$, $MgCO_3$, apatite, or ilmenite.

Also, early work used alkali metal salts of fatty acids, or soaps derived from natural oils by the process known as saponification. When an oil containing triglycerides is treated with a caustic solution under certain harsh processing conditions, the triglycerides disassociate into the alkali metal salts of the component fatty acids. The dissociation of the triglycerides into neutralized fatty acids is the saponification process. These neutralized fatty acids are soaps that act as non-selective flotation collectors.

Compounds containing sulfur, such as xanthates, thionocarbamates, dithiophosphates, and mercaptans, will selectively collect one or more sulfide minerals such as chalcocite, chalcopyrite, galena, or sphalerite. Unfortunately, sulfur based collectors are often toxic, have repugnant odors or both. Amine compounds are used to float KCl from NaCl and for silica flotation. Petroleum-based oily compounds such as diesel fuels, decant oils, and light cycle oils, are often used to float molybdenite. Those oils are also used as an "extender oil" that reduces the dosage of other more expensive collectors in the amine flotation of KCl.

Previous work on sulfide minerals has indicated that molecules containing sulfur are useful compounds for the froth flotation of sulfide minerals. These collectors are usually grouped into two categories: water-soluble and oily (*i.e.*, hydrophobic) collectors. Water-soluble collectors such as xanthates, sodium salts of dithiophosphates, and mercapto benzothiazole have good solubility in water (at least 50 gram per liter) and very little solubility in alkanes. Oily collectors, such as zinc salts of dithiophosphates, thionocarbamates, mercaptans, and ethyl octylsulfide, have negligible solubility in water and generally good solubility in alkanes.

Currently used collectors for most sulfide minerals are sulfur-based chemicals such as xanthates, thionocarbamates, dithiophosphates, or mercaptans. These chemicals have problems with toxicity and or repugnant odors. In addition,

these collectors can be very expensive. Therefore, a need exists for new collectors that are effective but not toxic or odiferous.

BRIEF SUMMARY OF THE INVENTION

This invention is directed to a method of beneficiating a mineral sulfide-containing material or a metallic species of gold, silver, copper, palladium, platinum, iridium, osmium, rhodium, and ruthenium by froth flotation in the presence of a collector as well as a collector for beneficiation of sulfide minerals, precipitates, or metallic species by froth flotation. In both aspects, the collector includes at least one oil which is either an essential oil or a natural or synthesized oil comprising triglycerides containing fatty acids of only 20 carbons or less, or an ester made from a fatty acid and an alcohol.

In the method aspect of the invention, the method includes the steps of (1) providing an aqueous slurry of the mineral sulfide-containing or metal-containing material, (2) adding a selective collector to the slurry, the collector comprising at least one oil selected from the group consisting of (a) a natural oil or synthesized oil comprising triglycerides containing fatty acids of only 20 carbons or less, or an ester made from a fatty acid and an alcohol; and (b) an essential oil; (3) selectively floating the mineral sulfide; and, then (4) recovering the mineral.

In the collector aspect of the invention, a collector is provided for beneficiation of sulfide minerals or precipitates from ores, concentrates, residues, tailings, slags, or wastes is provided. The collector includes at least one sulfur-containing sulfide mineral flotation promotor; and at least one oil selected from the group consisting of (1) a natural or synthesized oil comprising at least one triglyceride, or at least one ester made from a fatty acid and an alcohol; or (2) an essential oil.

This invention has the advantage that the specified triglyceride, specialty, or essential oil will selectively float sulfide minerals by itself or mixed with other collectors. This and other advantages will be apparent from the detail description of the invention that follows.

DETAILED DISCLOSURE OF THE INVENTION

The subject invention provides materials and methods useful in the recovery of minerals. These materials and methods are specifically applicable to froth flotation procedures; whereby, minerals are removed and recovered from complex mixtures of ores, residues, concentrates, slags, and wastes. The subject invention can be used in remediation processes to remove unwanted materials or may be used in mining processes to recover valuable minerals. Specifically exemplified herein is the use of certain triglycerides, esters of fatty acids and long chain alcohols, and essential oils of both terpene and aromatic chemistries. Any of these oils may be used alone, in mixtures of these oils, or in combination with other collectors.

In the method aspect of the invention, the method includes the steps of (1) providing an aqueous slurry of the mineral sulfide-containing or metal-containing material, (2) adding a selective collector to the slurry, the collector comprising at least one oil selected from the group consisting of (a) a natural oil or synthesized oil comprising triglycerides containing fatty acids of only 20 carbons or less, or an ester made from a fatty acid and an alcohol; and (b) an essential oil; (3) selectively floating the mineral sulfide; and, then (4) recovering the mineral.

In the collector aspect of the invention, a collector is provided for beneficiation of sulfide minerals or precipitates from ores, concentrates, residues, tailings, slags, or wastes is provided. The collector includes at least one sulfur-containing sulfide mineral flotation promotor; and at least one oil selected from the group consisting of (1) a natural or synthesized oil comprising at least one triglyceride, or at least one ester made from a fatty acid and an alcohol; or (2) an essential oil.

Preferably the mineral sulfide-containing material is selected from the group consisting of chalcocite, chalcopyrite, bornite, galena, sphalerite, pentlandite, molybdenite, and other sulfide minerals containing silver, gold, platinum, palladium, iridium, rhodium, and osmium, either in the crystal structure or in association as an independent mineral species, and combinations thereof.

This material may be derived from ores, concentrates, precipitates, residues, tailings, slag, or wastes.

Alternatively, the method may be carried out in the same steps except acting upon metallic species such as gold, silver, copper, palladium, platinum, iridium, osmium, rhodium, and ruthenium by froth flotation in the presence of a collector. The metallic species may be from material derived from any ore, concentrate, residue, tailings, slag, or waste.

The oils used according to the subject invention can be readily obtained and used by a person trained in the teaching of this patent. The natural oils identified in this invention are obtained directly or indirectly from plants or animals.

In a specific embodiment, the process of the subject invention can comprise the following steps:

a) pulverizing a mineral-containing material to appropriate fine-sized particles;

b) mixing the pulverized particles with water to produce a slurry;

c) agitating the mixture and adjusting its pH as necessary to produce a conditioned slurry;

d) adding a sufficient amount of a naturally occurring oil or a mixture thereof to the slurry with conditioning to render the surfaces of the particles containing the desired minerals hydrophobic;

e) agitating the resultant slurry under conditions and for a time sufficient to obtain a sufficiently homogenous mixture;

f) adding a frothing agent to the homogenous mixture in an amount sufficient to cause frothing of the homogenous mixture upon injecting air or other gases;

g) injecting air or other gas into the mixture to form bubbles in the resultant composition in an amount and under conditions sufficient to cause the hydrophobic particles to become attached to the bubbles and cause the resultant bubbles with attached particles to rise and form froth; and

h) separating the froth fraction and recovering the desired mineral.

In a specific embodiment of the subject invention, the mixture produced in Part (b) will have between about 1% to 75% solids by weight. In Part (c) of the

process, the pH may be adjusted to anywhere in the 5 to about 13 pH range, with particularly good results in the 7 to 10 pH range. With regard to Part (d), a natural oil, such as cottonseed, may be used as the only collector or it may be used with other collector compounds. In a preferred embodiment, the concentration of the natural oil used according to the subject invention can range from about 1 gram per ton of ore to about 1,000 grams per ton of ore. The temperature range of the use of these compounds goes from 5 to 75 degrees Centigrade with most normal operations in the 15 to 40 degree Centigrade range. Preferably, the flotation conditions should be kept mild enough to prevent significant disassociation of the triglycerides, or other components, contained in the natural oils into fatty acids, and to prevent the subsequent saponification into fatty acid soaps. The selectivity of the flotation when using oils according to this invention is evidenced by the selective recovery of the minerals, and substantiates this observation. A skilled artisan trained in the teachings of this patent can adjust the concentration and conditions to achieve optimization of the process for a particular mineral once a collector compound has been identified as useful for that mineral species.

Gold, silver and platinum metal group metals (platinum, palladium, rhodium, and iridium) are often associated with sulfide minerals. These metals may be also effectively collected by the oils described in this patent either alone or in combination with another collector.

The invention is specifically exemplified for the recovery of certain sulfide minerals. A skilled artisan, having the benefit of the instant disclosure, could readily adapt the process for the recovery and/or removal of a broad range of sulfide minerals, silver, gold or platinum group metals.

It was found, however, that there are unexpected benefits of using certain organic compounds containing no sulfur, no nitrogen and no phosphorous for selective froth flotation of certain sulfides. These molecules contain oxygen in a variety of functional groups such as triglycerides and esters. These groupings occur in many natural oils, such as cottonseed, corn, palm, safflower, jojoba, and clove. Surprisingly many of these oils are non-toxic and are used in foodstuffs

throughout the world. The oils run in price from $0.40 per kilogram to over $125 per kilogram.

It was also unexpected that blends of these oils with each other and with standard collectors frequently exhibit synergistic or enhanced effects, in that mixture of a sulfur containing collector with a non-sulfur containing collector may perform better than either of the components alone, and mixtures of multiple components may perform better than a two-component blend. This invention is uniquely suited to such mineral species as chalcocite, chalcopyrite, bornite, galena, and sphalerite. However, sulfur species such as pyrite are not as readily floated by these non-sulfur-containing collectors.

Most natural plant and animal oils are triglycerides of mixtures of fatty acids. A triglyceride is simply the reaction product of a carboxylic acid and glycerol. The general formula for a triglyceride is shown in Figure 1. Triglycerides are generally made from fatty acids with typically 10 to 24 carbon atoms and from 0 to 3 double bonds in their chains. Some triglycerides are made from hydroxyl fatty acids that have an alcohol group somewhere in the chain. An example of this is castor oil. Another oil, oiticicia, has three double bonds and a ketone functionality in its composition.

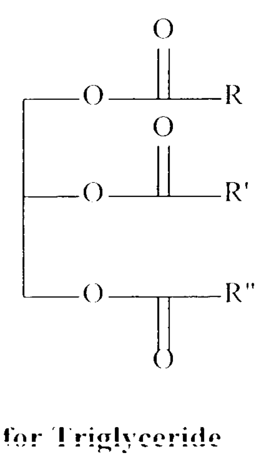


Figure 1. General Formula for Triglyceride

Saturated or highly saturated oils, such as coconut oil, contain triglycerides made from a zero or a low percentage of fatty acids with double bonds. Linseed oil contains a high percentage of linolenic acid oil, an 18 carbon fatty acid with

three double bonds (expressed as $C_{18:3}$). The composition of some common natural oils is shown in Table 1. The iodine value is a measure of the unsaturation of the oil. The saturated fat column is for the percentage of saturated fat when the exact chain length is unspecified. A given type of oil composition will vary with the variety of plant, the growing conditions and the treatment of the oil after pressing. For instance there are both high and low erucic acid ($C_{22:1}$) species of canola oil. Some canola oil is also hydrogenated (hydrogen reacted with the double bonds) before being sold.

It was unexpectedly found, however, that oils containing triglycerides that have fatty acids with 20 carbon atoms or less, perform much better than oils, such as canola oil, that contain triglycerides with fatty acids having 22 carbons or more, such as erucic acid ($C_{22:1}$). Moreover, since oils containing triglycerides of fatty acids with twenty carbon atoms or less do not contain free fatty acids, they do not behave as either fatty acids or soaps of fatty acids. The selective nature of these oils in flotation was surprising because fatty acids and fatty acid salts (i.e., soaps) are very non-selective.

Table 1 Composition of Common Vegetable Oils

Type	Iodine Value	Fatty Acids in Triglyceride Saturated Fat	C6:0	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1	Alcohol C18:1
Coconut	6-11		0.4	5.2	5.6	47.0	19.4	7.5	4.3	4.3	1.8		1.0				
Palm Oil typical	44-58						2.0	42.0	4.0	42.0	10.0						
Olive	75-94							15.0	75.0	10.0							
Castor	82-92						2.0	1.0	7.0	3.0							88.0
Apricot	81-123								5.5	66.0	27.0						
Corn Oil	103-133						0.2	11.8	2.0	24.1	61.7	0.7					
Cottonseed	103.9						1.4	29.8	3.3	30.4	42.9		0.8				
Soybean 1	120.9	12.0								60.0	25.0	2.9					
Soybean 2	124.9	13.2								34.0	49.1	3.6					
Soybean 3	127-140	12.5								28.6	52.8	6.8					
Sunflower	128							6.0	4.1	24.4	64.3						
Linseed	170-204							5.5	3.5	19.1	15.3	57.0					
Tung												85					
Avocado									14	70	15	1					

Other sources of triglycerides are animal oils. Commercially available animal oils have a limited range of unsaturation values. A highly unsaturated lard oil will have triglycerides containing 46% $C_{18:1}$ (oleic acid), 15% $C_{18:2}$ (linoleic acid), 1% $C_{18:3}$ (linolenic acid), and 62% saturated fatty acids.

There are some unique natural oils. Sperm whale oil is esters made from long chain fatty acids and long chain fatty alcohols instead of esters of the fatty acid and glycerol as in triglycerides. Both the fatty acid and long chain alcohol usually contains at least 1 double bond. Sperm whale oil is of course no longer available due to whaling restrictions. However, its replacements, jojoba oil (vegetable) and orange roughy oil (fish), have the same basic chemistry as sperm whale oil. The only differences between them are in the carbon numbers (chain length) of the various components of the oils.

Chemical manufacturers can synthesize a long chain ester from a fatty acid and a long chain alcohol. One example of a "synthesized oil" or "synthetic oil" is 2-butyloctyl oleic acid ester. This compound contains one unsaturated site in the fatty acid molecule. The carbon numbers of the largest fractions of these oils are shown in Table 2.

Table 2. Carbon Numbers of Major Components of Specialty Oils

	% of Material of Specified Carbon Number							
Oil	30	32	34	36	38	40	42	44
Sperm Whale	21	23	20	12				
Jojoba					6	31	50	8
Orange Roughy			11	16	25	23	15	5
2-butyloctyl oleic acid ester		100						

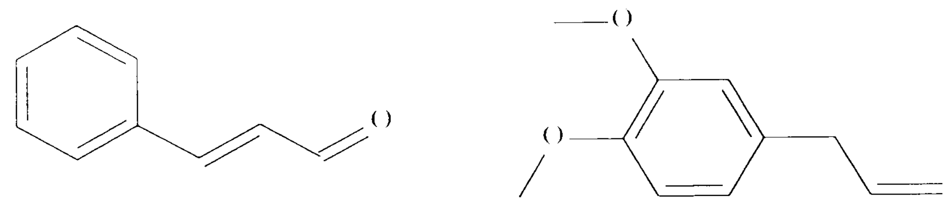
Preferably, the natural oils used in this invention include triglycerides that contain only fatty acids having a carbon number less than 20. Also, it is preferred that the triglycerides include an alcohol, an ether, an aldehyde, or a ketone functional group, or an aromatic group. A preferred group of natural oils includes cottonseed, corn, linseed, rice bran, safflower, soybean, avocado, jojoba, menhaden, lard, castor, cod liver, tung, oiticicia, apricot, sunflower, pistachio,

herring, and coconut oils. A more preferred group of natural oils includes cottonseed, corn, linseed, rice bran, safflower, soybean, avocado, jojoba, menhaden, lard, castor, cod liver, tung, and oiticicia. A still more preferred group of natural oils includes cottonseed, corn, linseed, rice bran, safflower, soybean, avocado, jojoba, menhaden, lard, and castor oils. An even more preferred group of natural oils includes cottonseed, corn, linseed, rice bran, safflower, and soybean. The most preferred natural oil is cottonseed oil.

Another class of naturally occurring oils is called "essential oils" or "volatile oils." These are fragrant oils derived from various plant species. Since ancient Egyptian times, they have been used for their fragrance and reputed medicinal properties. The chemistry of most of these compounds is based on either terpene chemistry or aromatic chemistry.

Terpene chemistry is defined as compounds that can be assembled from two or more moles of isoprene (C_5H_8) and the alcohol, aldehyde, and ketone derivatives of such compounds. A terpene compound can be defined as a monoterpene, sesquiterpene, or diterpene compound based on whether it contains 2, 3, or 4 isoprene units, respectively. Within each of these classifications the compounds can be further defined as being acyclic, monocyclic, bicyclic or tricyclic depending on whether the terpene contains, respectively, 0, 1, 2, or 3 ring structures (only diterpenes are tricyclic). Tricyclic diterpenes are generally solids.

Aromatic chemistry for essential oils is the chemistry of derivatives of benzene. The two most common aromatic components of essential oils are cinnamaldehyde and eugenol. These are obtained from cinnamon and clove oil. Their structures are shown in Figure 2.



Cinnamaldehyde Eugenol

Figure 2. Structure of Eugenol and Cinnamaldehyde

Most essential oils have one single major terpene or aromatic component or are a mixture of closely related terpenes or aromatics. Table 3 shows the composition of some representative essential oils. Note that any particular oil's composition can vary with variety, weather, etc.

Table 3. Major Constituent of Representative Essential Oils

		Major Component		
Oil	Plant Source	Name	%	Chemical Family
Citronella	Cymbopogon winterianus	Citronellal: Citronellol: Geraniol:	33 16 24	Aldehyde and Alcohols of acyclic monoterpene
Limonene	Citrus (Orange)	Limonene	95	Monocyclic monoterpene
Eucalyptus	Eucalyptus globus	Cinole	90	Bicyclic monoterpene ether
Sandalwood	Sandalwood	Mixture	80	Sesquiterpenes
Clove	Clove	Eugenol	85	Aromatic

Preferably, the essential oils used in the method of this invention include either a terpene compound or an aromatic compound. More preferably, the essential oil includes a terpene derivative having a functional group selected from an alcohol, an ether, an aldehyde, or a ketone. Specific preferred essential oils include limonene, citronella, eugenol, eucalyptus globus, camphor, and clove oil. A more preferred group of essential oils includes limonene and citronella.

As work with the triglycerides, esters and alcohols have indicated, other oxygen-containing compounds such as aldehydes, ketones, and ethers of sufficient

carbon number to be water-insoluble function as collectors for sulfide minerals. These compounds may or may not have carbon-carbon double bond(s).

The literature has shown that emulsified collectors can give better results than unemulsified collectors. Emulsification should also allow the combining of inexpensive water-soluble xanthates and sodium sulfide into the oils. Other water-soluble collectors that may be amenable to emulsification into oil include sodium dithiophosphates and mercaptobenzothiazole.

The invention also includes the use of the plant and animal oil collectors blended with known commercial collectors. Commercial collectors are also known as "flotation promotors" and are identified herein as "sulfur-containing flotation promotors." These common commercial promotors are usually separated into two classes of chemicals based on their water solubility. Water soluble sulfur containing collectors, or promotors, used in the froth flotation of sulfide minerals include such well-known collectors as xanthates and dithiophosphates. These are usually used as sodium or potassium salts of the respective organic acids. An example of a water-soluble collector would be sodium isopropyl xanthate. The other class of sulfur containing collectors would be water insoluble collectors. These collectors are generally referred to as oily collectors, because they are liquids that are insoluble in water. These collectors include thionocarbamates, mercaptans, organic sulfides, and the zinc salts of dithiophosphates. Even though these compounds are chemical reaction products, they are called oils.

Another grouping of collectors commonly used in froth flotation of substances such as coal, sulfur, and molybdenite are petroleum-based products that are truly oils. These oils generally consist of kerosene, vapor, diesel, fuel, turbine, light cycle, and carbon black oil. These petroleum oils are generally called "extender oils" and generally exhibit poor collecting ability and very poor selectivity when used by themselves. To distinguish these "petroleum-based collectors" from other described collectors, the term "oily collector" used in this text means a synthesized organic chemical compound containing sulfur such as the group of "sulfur-containing flotation promotors" described above.

This invention also includes the use of any of these aforementioned natural, synthetic or essential oils in combination. The essential oils are found to be very potent collectors. As such they are ideally suited for use in small amounts in combination with other oils or with other sulfide-containing flotation promotors. Good results have been obtained when using the essential oils in amounts of less than 10% by weight blended with other collectors. Preferably, less than 2% by weight is used.

Also, any of the natural oils including the higher carbon fatty acid-containing triglycerides, and in particular, the preferred natural oils alone or in combination with other preferred oils, may be used blended with any number of sulfur-containing flotation promotors. In such blends, the natural oils make up preferably between 20% and 80% by weight of the blend, and the flotation promotors make up preferably between the remaining 80% and 20% by weight of the blend. Optionally, a frother may be added to that blend, preferably in an amount between about 10% and 40% by weight of the composition. Frothers are commercially available compositions that are used to develop a froth or foam on top of a slurry that has been aerated. A particular suitable frother is one such as that sold by NALCO under the designation 9743. Methyl isobutyl carbonol (MIBC), also known as methyl amyl alcohol, is one of the most widely used frothers in the mining industry.

The collectors and blends of collectors in accordance with the methods of this invention can be used in standard froth flotation processes known by those skilled in the art and modified by the teachings of this patent as illustrated in the following examples.

EXAMPLES

The following are examples that illustrate procedures for practicing the invention. These examples should not be construed as limiting the invention, but are provided to further illustrate the teachings of the invention. All percentages are by weight and all collector mixture proportions are by volume unless otherwise noted.

Example I.

This example is the effectiveness of cottonseed oil as a collector for molybdenite and chalcopyrite. The ore had a head grade of 0.259% Cu and 0.0064% Mo. The ore charge of 1.0 kilogram was ground at 60% solids to 60% passing (P60) a 150 micron (100 mesh) screen. The ground ore slurry was adjusted to a pH of 10.5 with lime. The ore was ground with 10 gram/ton (0.020 pound/ton) of secondary collector. A Denver laboratory flotation machine was used. The ore slurry charge was diluted with water to 29 percent solids, and 6 grams per ton of the main collector, sodium ethyl xanthate, and 25 gram/ton (0.05 pound/ton) of the OrePrep F-533 frother were added. The flotation was carried out for a total of six minutes with a two minute break for conditioning at the halfway point. During the conditioning break, 4 gram/ton dosage of the sodium ethyl xanthate was added.

The cottonseed oil was used by itself in place of the standard decant oil-light cycle oil-mercaptan (tertiary dodecyl mercaptan) secondary collector. Also, a 33% each mixture of cottonseed oil, zinc di (1,3 dimethylbutyl) dithiophosphate, and the tertiary dodecyl mercaptan was tested. For comparison a 33% each mixture of decant oil, the zinc dithiophosphate and the mercaptan was tested. The dosage of the main and secondary collector was 10 grams collector per ton of ore (g/t) for all tests. As shown in Table 4, cottonseed oil by itself improved the recovery of both molybdenum recovery and copper grade over the standard collector. The cottonseed mixture had a simiiar copper recovery as the decant oil mixture while improving copper grade.

Table 4. Chalcopyrite Ore containing MoS_2 Flotation

Main Collector	Secondary Collector	Cu Recovery	Cu Grade	Mo Recovery
Xanthate	Cottonseed Oil	94.5%	3.68	82.2%
Xanthate	Standard	93.9%	2.96	79.1%
Xanthate	Decant Oil Mixture	97.0%	2.85	87.3%
Xanthate	Cottonseed Mixture	96.2%	4.25	83.7%

Example II.

This example shows that cottonseed oil can be used to collect some galena (PbS). It can be used either alone in place of the main collector, sodium isopropyl xanthate, or in a mixture with a mercaptan (tertiary dodecyl mercaptan) collector in place of the main collector.

The ore was ground to a P80 of around 240 microns. The ore charge was 2.0 kilograms and had a head assay of 70 gram/ton Ag, 0.70% Pb, and 1.32% Zn. Fifty gram/ton of zinc sulfate and fifteen gram/ton of dextrin were added to the grind. The flotation was conducted in a Denver laboratory flotation machine with a 5-liter cell. The float was conducted at the natural pH of the ore, 7.5 to 8. Before the first float, the slurry was conditioned with 30 gram/ton of the collector and 80 gram/ton of the frother for two minutes. The ore was floated for three minutes, then conditioned with 10 gram/ton collector and 16 gram/ton of frother. The results are shown in Table 5, and demonstrate the enhanced effects for a blend of the natural oil and the mercaptan flotation promotor in comparison to the use of each alone.

Table 5. Lead-Zinc-Silver Sulfide Ore Flotation for Lead

	Grade		Recovery into Pb Concentrate				
Collector	Pb	As	Weight	Ag	Pb	Zn	Fe
Xanthate	2.18	1.23	23.6%	74.9%	79.5%	18.0%	82.9%
Cottonseed Oil	6.38	0.49	5.1%	51.4%	50.6%	17.2%	15.7%
Mercaptan	7.08	0.76	5.7%	42.9%	49.1%	19.3%	14.7%
50% Mercaptan + 50% Cottonseed	3.21	0.78	13.8%	53.9%	64.5%	21.1%	38.6%

The ore was then conditioned for two minutes with 125 gram per ton of copper sulfate. A further 10 gram/ton of collector and 32 gram/ton of frother were added and conditioned in for two minutes. The first zinc float was conducted for three minutes. Finally, another 50 gram/ton of frother was added. The results of these zinc floats are shown in Table 6.

Table 6. Lead-Zinc-Silver Sulfide Ore Flotation for Zinc

	Grade	Recovery into Zn Concentrate				
Collector	Zn	Weight	Ag	Pb	Zn	Fe
Xanthate	8.63	9.5%	16.5%	7.1%	42.1%	6.3%
Cottonseed Oil	9.13	6.6%	13.9%	20.4%	48.1%	10.1%
Mercaptan	12.20	5.6%	16.7%	19.8%	46.4%	6.2%
50% Mercaptan + 50% Cottonseed	11.54	5.0%	9.1%	7.1%	45.6%	3.8%

Example III.

Apricot, sunflower, pistachio, cottonseed, and jojoba oils were tested on chalcopyrite ore containing molybdenum sulfide. The head assays of the ore were 0.704% Cu and 0.0119% Mo. The ore charge of 2.0 kilograms was ground at 65% solids to 90% passing a 212 micron (65 mesh) screen. The ore charge was diluted with water to 27% solids and placed in a Denver laboratory flotation cell. The ore was conditioned for two minutes by agitation at 2000 rpm. The ore was floated for one minute by allowing air to be drawn in by the impeller. Subsequently, the ore was conditioned for two minutes, floated for two minutes, conditioned for two minutes, and finally floated for three minutes. The standard collector is a mixture

of 33% of the allyl ester of isopropyl xanthate, 33% of 2-ethylhexanol, and 33% of sodium diisobutyl di-thiophosphate collector.

The standard reagent addition is as follows. Enough lime is added to the ball mill to adjust to a pH of 10.4. At the same time, 7.7 gram/ton (0.0154 pound/ton) of the standard collector or oil being tested, 7.5 gram/ton (0.0150 pound/ton) of diesel fuel are added. During the first conditioning step, 20 g/t (0.040 lb/ton) of frother is added. During the second conditioning step, 8 g/t (0.016 pound/ton) of sodium isopropyl xanthate (SIPX), 2.5 g/t (0.005 lb/t) of frother, and 5 g/t (0.010 lb/ton) of the standard reagent or oil are added. During the third and final conditioning step, 4g/t (0.008 lb/ton) of SIPX, (0.005 lb/t) of frother, and 5 g/t (0.010 lb/ton) of the standard reagent or oil are added.

The results for the final combined concentrates are presented in Table 7, sorted by copper recovery. Every oil listed above the sunflower oil gave essentially the same copper and molybdenum recovery as the standard reagent.

Table 7. Chalcopyrite Ore containing MoS_2 Flotation

Tested Oil	Cu Grade	Recovery Cu	Recovery Mo
Standard	5.04	92.4%	84.6%
Cottonseed	3.62	91.9%	84.4%
Pistachio	2.92	91.9%	88.3%
Sunflower	2.97	91.8%	84.7%
Apricot	2.70	91.7%	79.6%
Jojoba	2.69	91.5%	86.5%

Example IV.

There are two primary types of cotton in the United States, Pima long staple cotton and short staple cotton. The oils derived from both were tested on a copper-molybdenum ore with a head grade of 0.663% Cu and 0.0134% Mo. The ore was floated as in Example III. The results of the test are shown in Table 8.

Table 8. Comparison of Cottonseed Oils

Cottonseed Oil Source	Grade Cu	Recovery Cu	Recovery Mo
Pima Long Staple	5.36	94.8%	84.7%
Short Staple	5.23	90.9%	83.9%
Standard Collector	5.76	90.6%	82.1%

Example V.

This example shows the selectivity of cottonseed against calcite. Pure calcite crystals were crushed and screened for the fraction passing a 355 micron (42 mesh) screen. A sample size of 812 grams was obtained. The sample was slurried in a 2.5 liter cell of a Denver laboratory flotation machine. The ore was conditioned for two minutes with 123 gram/ton cottonseed oil and 26.2 gram/ton frother. The slurry was floated for two minutes and then conditioned again for two minutes with 61.5 gram/ton cottonseed oil and 10.5 gram/ton frother. The slurry was floated again for two minutes. During both flotations, a slime-stabilized froth was obtained. The results of the test are shown in Table 9.

Table 9. Recovery of Calcite from Pure Calcite Sample Float

Concentrate	Recovery
1	10.70%
2	1.88%
Combined	12.58%

Example VI.

This example shows cottonseed's selectivity against silica. Pure quartz crystals were crushed and screened for the fraction passing a 150 micron (100 mesh) screen. A sample size of 1000 grams was obtained. The sample was slurried in a 2.5 liter cell of a Denver laboratory flotation machine. The ore was conditioned for two minutes with 123 gram/ton cottonseed oil and 26.2 gram/ton frother. The slurry was floated for two minutes and then conditioned again for two minutes with 61.5 gram/ton cottonseed oil and 10.5 gram/ton frother. The slurry was floated again for two minutes. During both flotations, a small amount

of slime-stabilized froth was obtained. The total recovery was less than 2% of the total silica.

Example VII.

A number of triglyceride, specialty, and essential oil collectors were tested on chalcopyrite ore containing molybdenite. The head assays of the ore were 0.579% Cu and 0.010% Mo. The ore charge of 1.0 kilograms was ground at 65% solids to 90% passing a 212 micron (65 mesh) screen.

The standard flotation procedure was as follows. Enough lime (0.9 grams) was added to the grind for the flotation slurry to have a pH of 10.4. The following reagents were added to the grind. 5.5 gram/ton of the standard thiophosphate copper collector, 7.7 gram/ton of diesel fuel, molybdenum collector, and 10 gram/ton of Nalco 9743 frother. A Denver laboratory flotation cell was used. The ore charge was diluted with water to 27% solids. The ore was floated for two minutes. The slurry was then conditioned for one minute with 6.5 gram/ton of frother and 8 gram/ton of sodium isopropyl xanthate. The slurry was floated for two more minutes, then conditioned for one more minute with half of the dosage of the previous conditioning step, and floated for a final three minutes. All concentrates were collected into one pan for a single concentrate for the whole flotation.

The oils were tested by using them as the only collector. Only lime, 10 grams/ton of frother and 24 gram/ton of the oil being tested were added to the grind. No xanthate or other collector was added to the conditioning step, only the listed frother dosage.

The results for the triglyceride tests are presented in Table 10. As tested, no triglyceride was as good a collector for copper as the standard collector system. Due to the low molybdenum grade of the head ore, molybdenum recoveries often have a large standard deviation in repeated tests on the same ore. Generally, compounds that show a 5% better recovery than another compound in single tests will have an average higher molybdenum recovery on multiple tests.

Table 10. Results of Triglycerides Flotation

Collector	Number of Double Bonds, % 0	1	2	3	5	Assay Con Cu	Mo	Recovery Cu	Mo
Standard						4.94	0.071	88.3%	79.2%
Cottonseed	27	30	43	0		3.82	0.063	87.3%	84.7%
Lard Oil	31	48	12	1		5.61	0.094	85.4%	80.9%
Corn	13	29	57	1		5.64	0.084	85.3%	81.6%
PBO Lard	38	46	15	1		5.01	0.082	85.2%	83.4%
Linseed	9	19	15	57		4.91	0.080	85.1%	80.2%
Tung				85		5.71	0.088	85.1%	78.2%
Menhaden	18	18	37	13	14	8.52	0.144	84.5%	80.7%
Safflower	21		79			3.75	0.071	84.2%	83.9%
Herring	14	49			23	7.88	0.122	84.0%	78.9%
Avocado		70	15	1		6.38	0.111	84.0%	85.0%
Oiticicia [1]				75		4.63	0.074	83.8%	78.2%
Soybean	16	24	54	7		5.14	0.094	83.7%	80.2%
Peanut	15	45	40	0		8.33	0.142	82.8%	81.3%
Castor [2]	12	88				7.20	0.122	82.2%	77.9%
Canola	8	59	22	11		8.43	0.130	82.0%	80.6%
Rice Bran	64	2	32	2		8.02	0.142	81.5%	78.7%
Coconut	94	4	2			7.38	0.133	74.1%	75.0%

Notes: [1] Has a ketone functionality; [2] has a alcohol functionality

The results of the testing of specialty and essential oils are shown in Table 11. The bicyclic compounds equaled or surpassed the standard for copper and molybdenum recovery.

Table 11. Results of Specialty and Essential Oil Testing					
		Grade		Recovery	
Oil	Chemical Family	Cu	Mo	Cu	Mo
Eucalyptus globus	Bicyclic Ether	5.25	0.088	88.8%	87.8%
Standard	Thiophosphate	4.94	0.071	88.3%	79.2%
Camphor	Bicyclic Ketone	5.32	0.082	87.9%	85.7%
2-butyloctyl oleic acid ester	Mono-unsaturated Ester	5.62	0.092	87.3%	86.0%
Jojoba	Di-unsat. Ester	5.11	0.088	85.7%	84.8%
Limonene	Cyclic monoterpene	4.87	0.082	84.7%	81.2%

Example VIII.

A number of triglyceride, specialty, and essential oil collectors were tested on a molybdenum sulfide ore. The head assay of the ore was 0.0638% Mo. The ore charge of 1.0 kilogram was ground at 65% solids to 90% passing a 425 micron (35 mesh) screen.

The flotation procedure is as follows. The 100 gram/ton of oil was added to the grind. A Denver laboratory flotation cell was used. The ore charge was diluted with water to 27% solids. To the two minute conditioning step, 40 g/t frother was added. The ore was floated for 1 minute. The slurry was then conditioned for one minute, floated for two minutes, conditioned for one minute, and finally floated for six minutes. Each concentrate was collected separately and assayed separately. One test was conducted with frother alone to test the free flotability of the ore. The standard collector used at the mine was diesel fuel.

The results of the flotation of molybdenum sulfide for the triglycerides are shown in Table 12. The percentage of fatty acids in the triglycerides with the shown number of double bonds is listed. All of these oils did better than the free-flotability test

Table 12. Results of Triglycerides on Molybdenum Recovery

	Number of Double Bonds, %					1^{st} Concentrate		Overall	
Collector	0	1	2	3	5	Grade	Recovery	Grade	Recovery
Oiticicia[1]				75		2.19	68.9%	0.892	72.5%
Peanut	15	45	40	0	0	1.15	57.9%	0.602	71.9%
Coconut	94	4	2			9.42	60.1%	1.355	67.5%
Menhaden	18	18	37	13	14	4.14	59.0%	0.938	66.8%
Pfau 1JJ	31	48	12	1		3.11	54.9%	0.736	64.9%
Rice Bran	64	2	32	2		2.21	48.7%	0.763	61.4%
Cottonseed	27	30	43	0		4.44	51.1%	1.084	60.1%
Tung				85		3.57	54.8%	0.989	59.1%
Sunflower	12	24	64			3.21	48.8%	0.736	58.1%
None	0	0	0	0	0	3.38	53.9%	0.870	57.8%
Corn Oil	31	48	12	1		4.15	54.2%	1.013	57.7%
Linseed	9	19	15	57		2.61	48.4%	0.570	56.2%
Diesel	0	0	0	0	0	1.38	53.3%	0.565	56.1%

Notes: [1] Has a ketone functionality

The results of specialty and essential oils are shown in Table 13. All of these oils did better than the free-flotability test.

Table 13. Results of Testing Specialty and Essential Oils on Molybdenite

		First Concentrate		Overall	
Collector	Type	Grade	Recovery	Grade	Recovery
2-butyloctyl oleic acid ester[1]	Mono-unsaturated Ester	0.73	71.6%	0.589	80.2%
Jojoba	Di-unsat. Ester	0.96	68.5%	0.507	78.1%
Clove Oil	Aromatic	2.08	73.5%	0.817	77.9%
limonene oil	Cyclic monoterpene	2.24	75.0%	0.902	76.7%
Citronella	Acylic monoterpenes	2.00	69.8%	0.598	74.6%
Eucalyptus. globus	Bicyclic Ether	2.77	67.0%	0.759	71.6%
Camphor	Bicyclic Ketone	4.41	61.0%	1.056	64.9%
None		3.38	53.9%	0.870	57.8%
Diesel		1.38	53.3%	0.565	56.1%

Note: [1] Oil synthesized from natural products and used as a sperm whale oil replacement

Example IX.

In this example the synergistic effect of various oils and a sodium isopropyl xanthate is shown. A chalcocite ore with a head assay of 0.602% Cu and 0.016% Mo was used. The ore charge of 1.0 kilogram was ground at 65% solids to 90% passing a 212 micron (65 mesh) screen.

The standard flotation procedure is as follows. Enough lime (1.9 grams) was added to the grind for the flotation slurry to have a pH of 10.8. To this grind 30 g/ton (0.060 lb/ton) of either the standard collector, Cytec S-8399, believed to be a blend of dithiophosphate and thionocarbamate available from Cytec, Inc., Wayne, New Jersey, U.S.A., or the natural oil collector being tested was added. The grind charge was transferred to a Denver laboratory flotation cell. The ore charge was diluted with water to 27% solids. The ore was conditioned for two minutes with 20 gram/ton of Oreprep F-533, a blended alcohol frother. The ore was floated for three minutes. The slurry was then conditioned for three minutes with 10 gram/ton of frother and 1.5 gram/ton of sodium isopropyl xanthate (SIPX). The slurry was floated three more minutes. The concentrates were collected separately except for the avocado oil and Cytec S-8399.

The results are shown in Table 14. These results show that limonene oil has the best synergy with SIPX despite not collecting much chalcocite by itself as shown in the recovery in the first concentrate (1^{st} Con). All the oils performed better as a secondary collector than the regular thiophosphate based Cytec S-8399.

Table 14. Results of Tests with Oils and SIPX

	Overall			1st Con				
	Copper		Mo	Copper		Mo	Calc Head	
Collector	Grade	Recovery	Recovery	Grade	Recovery	Recovery	Cu	Mo
Limonene	5.50	92.2%	71.7%	2.02	9.98%	59.00%	0.599	0.0162
Safflower	5.23	92.2%	68.2%	1.11	6.26%	55.24%	0.604	0.0168
Coconut	5.77	92.1%	72.2%	1.95	8.67%	49.50%	0.608	0.0179
Eucalyptus	6.00	92.0%	65.9%	2.48	8.09%	39.14%	0.619	0.0154
Avocado	5.63	91.9%	65.9%				0.660	0.0157
Corn	4.90	91.9%	69.0%	2.13	11.42%	52.23%	0.571	0.0164
Cottonseed	5.57	91.7%	71.0%	2.76	12.66%	56.19%	0.590	0.0165
Tung	4.83	91.2%	67.1%	1.39	4.61%	42.21%	0.604	0.0167
S-8399	3.69	90.6%	69.5%				0.599	0.0148

Example X.

In this example, the various combinations of oils and standard collectors are shown. A chalcocite ore with a head assay of 0.543% Cu and 0.014% Mo was used. The ore charge of 1.0 kilograms was ground at 65% solids to 90% passing a 212 micron (65 mesh) screen.

The standard flotation procedure was as follows. Enough lime (1.9 grams) was added to the grind for the flotation slurry to have a pH of 10.8. To this grind 30 g/ton (0.060 lb/ton) of either the standard collector, Cytec S-8399, or the natural oil collector being tested was added. The grind charge was transferred to a Denver laboratory flotation cell. The ore charge was diluted with water to 27% solids. The ore was conditioned for two minutes with 20 gram/ton of Oreprep F-533 frother. The ore was floated for three minutes. The slurry was then conditioned for two minutes with 1.5 gram/ton of sodium isopropyl xanthate (SIPX). The slurry was floated three more minutes.

The mixtures tested are shown in Table 15. The mercaptan used was tertiary dodecyl mercaptan. The zinc dithiophosphate used was zinc di- (1,3 dimethylbutyl) -dithiophosphate. The thionocarbamate used was n-ethyl, o-isopropropyl thionocarbamate.

Table 15. Composition of Mixture Tested

Collector	Staple Type of Cottonseed	Percentage of Cottonseed	Mercaptan	Zinc dithio-phosphate	Thiono-carbamate	Glycol Still Bottoms
Mixture 1	Pima Long	40	40	10	10	0
Mixture 2	Short	40	40	10	10	0
Mixture 3	Short	20	20	20	20	20
Mixture 4	Short	50	10	30	10	0

The results of the flotation tests are summarized in Table 16. The results show that cottonseed interacts well with the mercaptan, zinc dithiophosphate and thionocarbamate collectors.

Table 16. Test results for Various Mixtures

	Overall Results			Calc. Head	
Collector	Grade	Cu	Mo	Cu	Mo
Mixture 3	4.48	90.4%	72.1%	0.532	0.0144
Mixture 1	4.99	89.6%	69.4%	0.562	0.0144
Mixture 2	5.48	88.8%	67.8%	0.544	0.0142
S-8399	4.88	88.6%	65.0%	0.525	0.0137
Mixture 4	5.75	88.1%	67.9%	0.583	0.0142

Example XI.

Pure mineral samples of chalcopyrite, chalcocite and galena were floated with cottonseed and limonene oils.

The flotation procedure was as follows: 500 gram charges of mineral were crushed to minus 1.7 millimeter (10 mesh) then ground with 50 gram per ton of collector to around 90% passing 212 micron (65 mesh). A charge was then placed in a Denver laboratory flotation cell with enough water to make the slurry 27% by weight solids. The slurry was then conditioned with 18 grams/ton of an alcohol frother for two minutes. The ore was floated for two minutes. The slurry was then conditioned for one minute and floated for three minutes. Each concentrate was collected and weighed separately. One test was conducted with frother alone to test the free flotability of the mineral. The results are shown below.

Table 17. Results of Pure Mineral Flotation

Collector	Chalcocite Con 1	Chalcocite Con 2	Chalcocite Total	Chalcopyrite Con 1	Chalcopyrite Con 2	Chalcopyrite Total
None	---	1.20%	1.20%	4.90%	3.31%	8.20%
Cottonseed	2.51%	1.87%	4.38%	58.75%	5.74%	64.49%
Limonene	3.59%	2.05%	5.64%	19.15%	4.70%	23.85%

Collector	Galena Con 1	Galena Con 2	Galena Total
None	18.98%	2.55%	21.54%
Cottonseed	90.95%	5.57%	96.52%
Limonene	18.53%	2.07%	20.60%

The cottonseed oil collected a good proportion of the pure mineral chalcopyrite. Comparing the results of cottonseed on chalcopyrite to the results of the "no collector" test shows that the cottonseed was responsible for collecting the chalcopyrite and that it is a better collector than the limonene oil.

Of course, it should be understood that changes and modifications can be made to the preferred embodiments described above without departing from the scope of the present invention. It is therefore intended that the foregoing detailed description be regarded as illustrative rather than limiting, and that it be understood that it is the appended claims including all equivalents, which are intended to define the scope of this invention.